Electronic Supplementary Material (ESI) for Nanoscale.

Strongly Coupled Plasmonic Metal Nanoparticles with Reversible pH-Responsiveness and Highly Reproducible SERS in Solution

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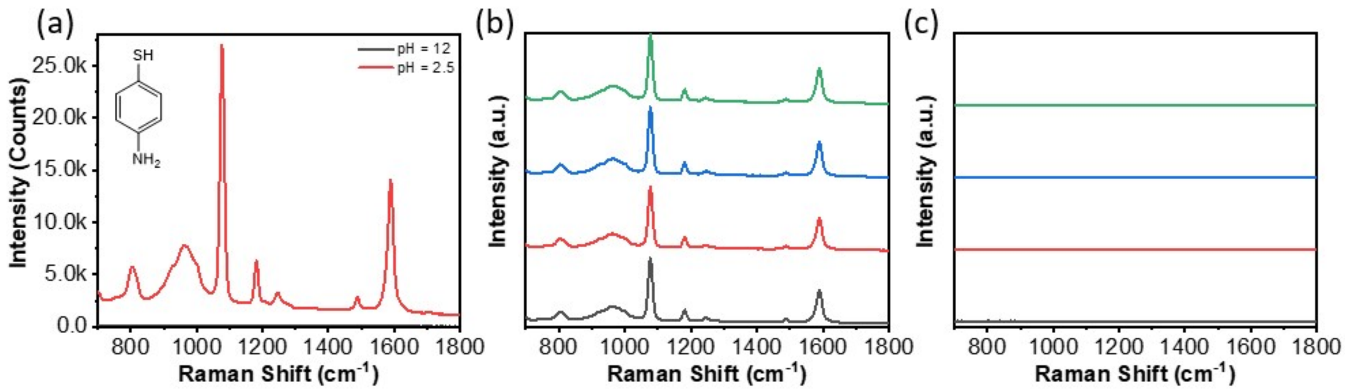

Figure S1. (a) SERS response of PAA-grafted AgNPs for 4-aminothiophenol at pH of 2.5 and 12. (b) Repeating SERS response of 4-aminothiophenol at a concentration of 1.0 µM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of 4-aminothiophenol at a concentration of 1.0 µM with PAA-AgNPs at pH of 12.

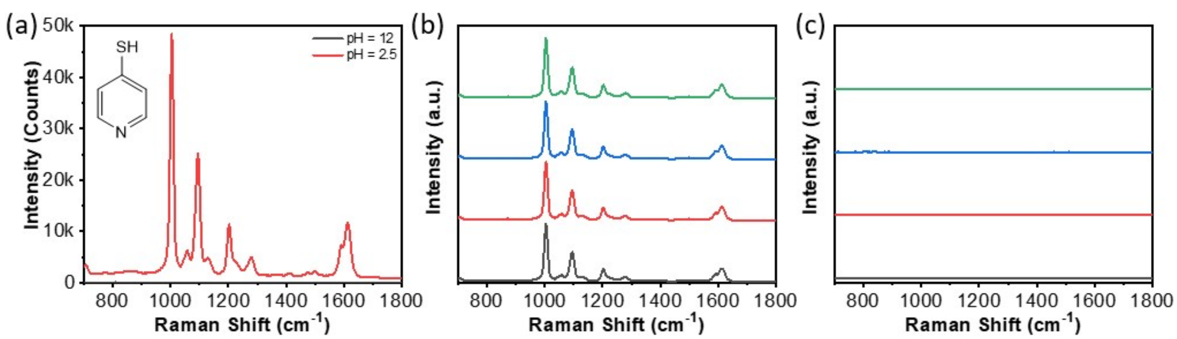

Figure S2. (a) SERS response of PAA-grafted AgNPs for 4-mercaptopyridine at pH of 2.5 and 12. (b) Repeating SERS response of 4-mercaptopyridine at a concentration of 1.0 µM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of 4-mercaptopyridine at a concentration of 1.0 µM with PAA-AgNPs at pH of 12.

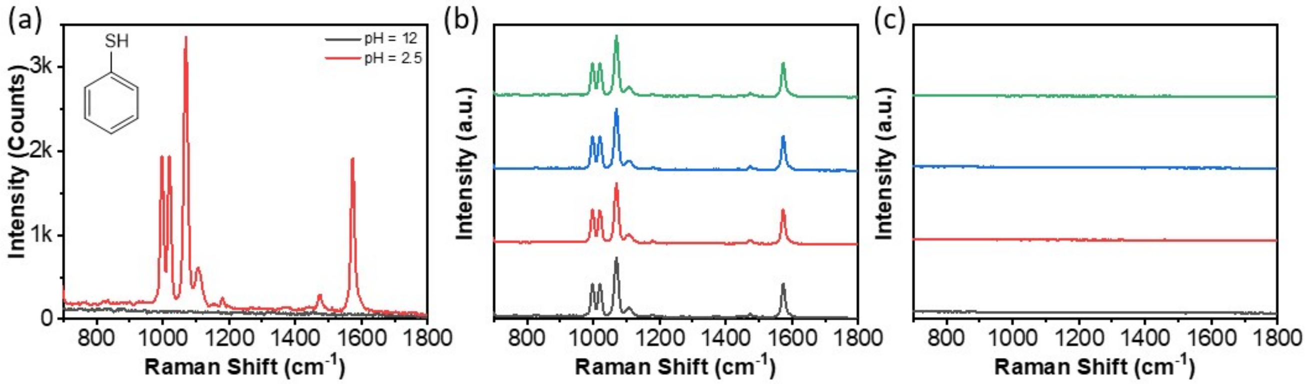

Figure S3. (a) SERS response of PAA-grafted AgNPs for thiophenol at pH of 2.5 and 12. (b) Repeating SERS response thiophenol at a concentration of 1.0 μM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of thiophenol at a concentration of 1.0 μM with PAA-AgNPs at pH of 12.

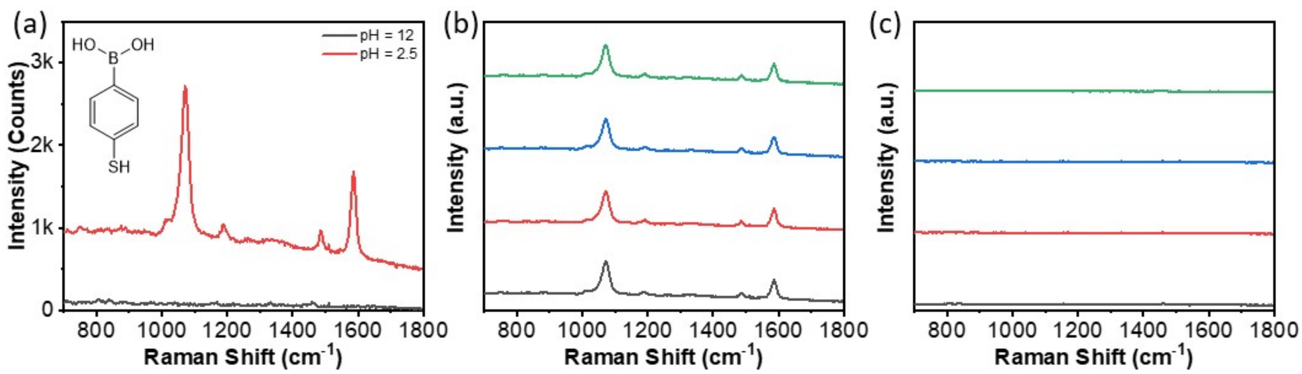

Figure S4. (a) SERS response of PAA-grafted AgNPs for 4-mercaptophenylboronic acid at pH of 2.5 and 12. (b) Repeating SERS response 4-mercaptophenylboronic acid at a concentration of 1.0 μM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of 4-mercaptophenylboronic acid at a concentration of 1.0 μM with PAA-AgNPs at pH of 12.

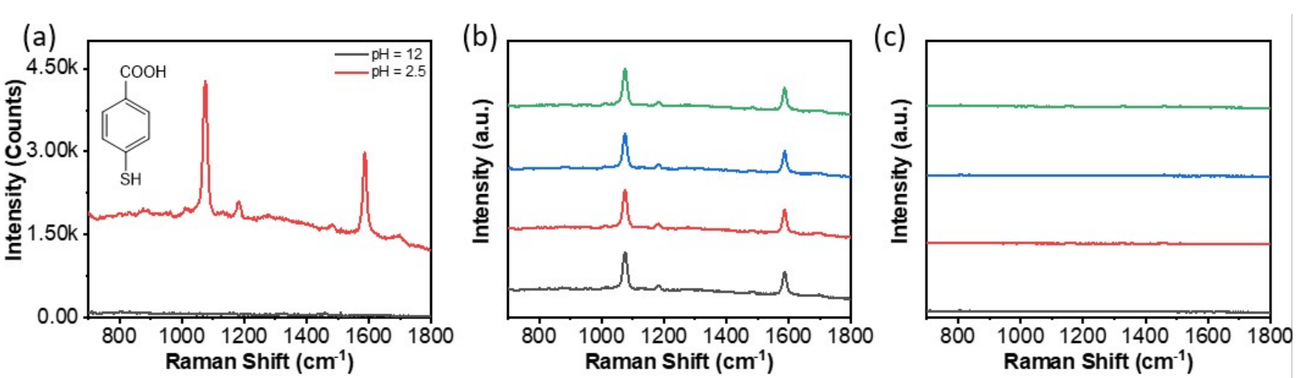

Figure S5. (a) SERS response of PAA-grafted AgNPs for 4-mercaptobenzoic acid at pH of 2.5 and 12. (b) Repeating SERS response 4-mercaptophenylboronic acid at a concentration of 1.0 μM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of 4-mercaptophenylboronic acid at a concentration of 1.0 μM with PAA-AgNPs at pH of 12.

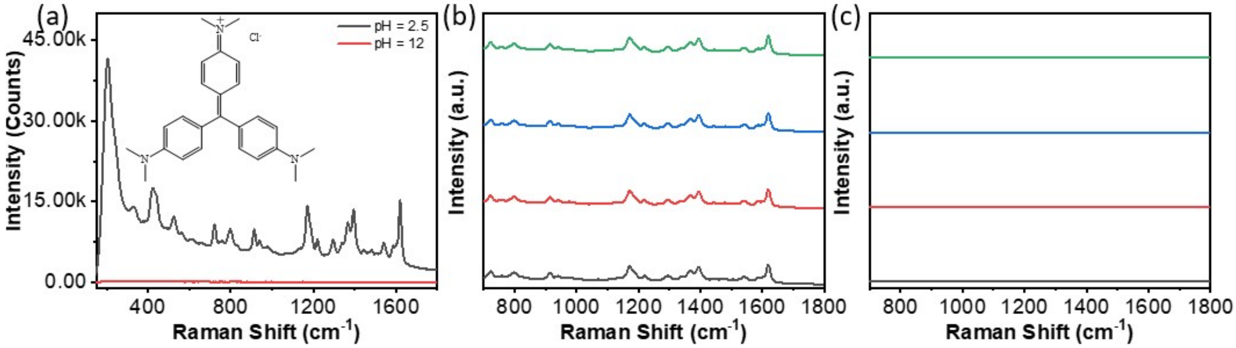

Figure S6. (a) SERS response of PAA-grafted AgNPs for crystal violet at pH of 2.5 and 12. (b) Repeating SERS response crystal violet at a concentration of 0.4 µM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of crystal violet at a concentration of 0.4 µM with PAA-AgNPs at pH of 12.

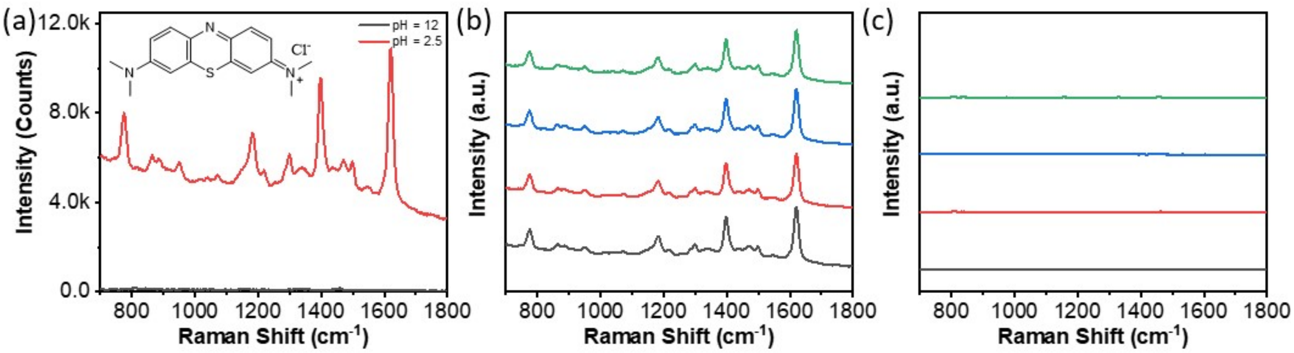

Figure S7. (a) SERS response of PAA-grafted AgNPs for methylene blue at pH of 2.5 and 12. (b) Repeating SERS response methylene blue at a concentration of 0.4 µM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of methylene blue at a concentration of 0.4 µM with PAA-AgNPs at pH of 12.

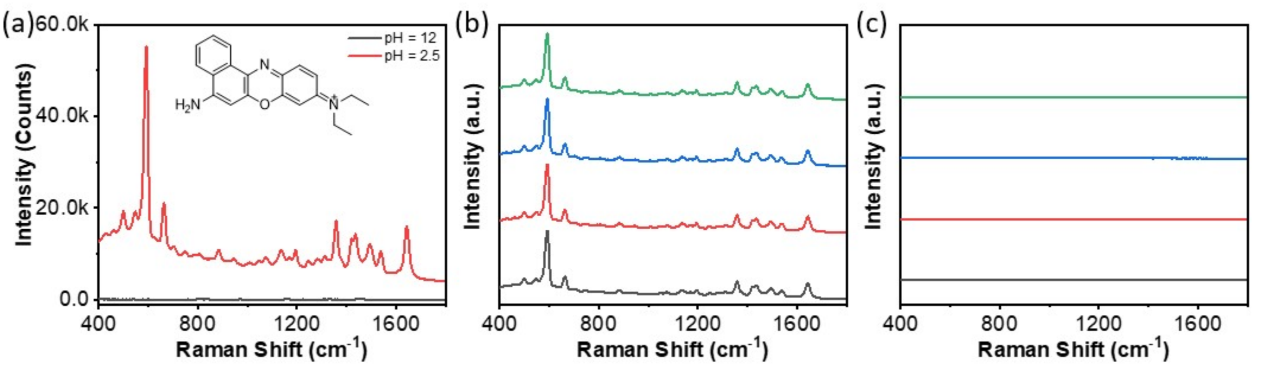

Figure S8. (a) SERS response of PAA-grafted AgNPs for Nile blue at pH of 2.5 and 12. (b) Repeating SERS response Nile blue at a concentration of 0.4 µM with PAA-AgNPs at pH of 2.5. (c) Repeating SERS response of Nile blue at a concentration of 0.4 µM with PAA-AgNPs at pH of 12.

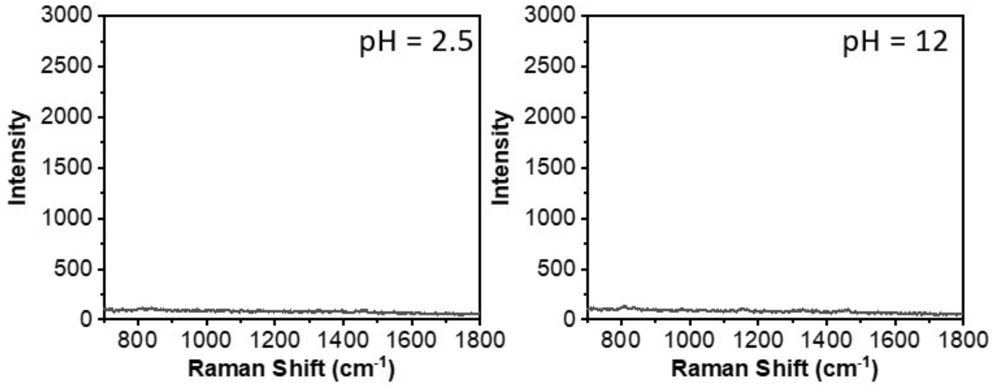

Figure S9. Raman spectra of PAA-AgNPs at pH of 2.5 and 12.

Calculation of limit of detection (LOD)
LOD is calculated from the slope of the calibration cure and the standard deviation. The formula is:

$$LOD = N \times \frac{SD}{S}$$

Where N is the signal-to-noise ratio (~ 3.3), S is the slope of the linear fitting and SD is the standard deviation.
For example, in Figure 4, the slope of the calibration curve is 0.58 and the SD is 0.058, then the LOD is

$$LOD = 3.3 \times \frac{0.058}{0.58} = 0.33\ \mu M = 3.3 \times 10^{-7}\ M$$

SAXS Model

Core-shell spherical model:

The intensity $I(q)$ for the core-shell spherical is given by:

$$I(q) = \frac{scale}{V} \times F(q)^2 + background,$$

where

$$F(q) = \frac{3}{V_s}\left[V_c(\rho_c - \rho_s)\frac{\sin(qR_c) - qR_c\cos(qR_c)}{(qR_c)^3} + V_s(\rho_s - \rho_{solv})\frac{\sin(qR_s) - qR_s\cos(qR_s)}{(qR_s)^3}\right],$$

where V_s and V_c are the volume of the whole particle and core, respectively. R_s and R_c are the radius of particles (radius plus thickness) and core radius, respectively. ρ_c, ρ_s, ρ_{solv} are the scattering length density of the core, the shell and the solvent, respectively.